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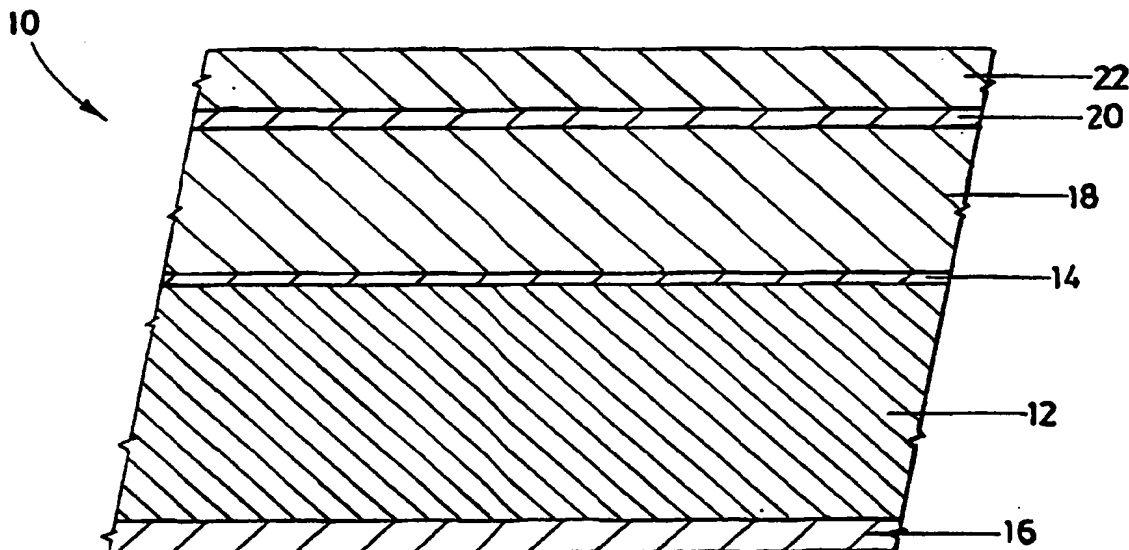
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## (57) Abstract

A multilayer heat-sensitive material for thermal imaging and preparation thereof are described (10). The material comprises a color-forming layer (18) containing a color-forming amount of a finely divided, solid, colorless noble metal or iron salt of an organic acid; a color-developing amount of cyclic or aromatic organic reducing agent, which at thermal copy and printing temperature is capable of a color-forming reaction with the metal salt; an image toning agent; and a carrier composition in which the noble metal or iron salt, organic reducing agent, and toning agent are distributed. The carrier composition comprises a substantially water-soluble polymeric carrier and a dispersing agent. The material also comprises a protective, clarifying, overcoating layer (22).

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## THERMAL IMAGING MATERIAL AND PREPARATION

### Field of the Invention

The present invention is directed to heat-sensitive materials, for example, film or paper-based materials, and the preparation of such materials using aqueous coating compositions, to form color-forming layers. The materials are particularly well suited for use in infrared copy and direct thermal printing devices.

### Background of the Invention

In recent years, direct thermal imaging by thermal imaging printers has become a popular method for recording documents and data because of the low cost and reliability of equipment. Infrared imaging is also a convenient and inexpensive way to produce monochrome thermal transparencies for overhead projector presentations. Technology commonly used for direct thermal printing devices is well known, as described, for example, in United States Patent Nos. 4,289,535 and No. 4,675,705 where colorless or pale colored chromogenic dyestuffs are combined with color-developing agents such as benzyl-p-hydroxy benzoate or 4,4'-isopropylidenediphenol. This technology, however, is not well suited for the manufacture of single sheet, transparent films for overhead projection presentations. The technology commonly used to produce single sheet, transparent black image films is also well known, as described, for example, in several United States patents including U.S. Patent Nos. 3,080,254, 3,031,329, 3,446,648 and 5,026,606, in which a noble metal salt of an organic acid, preferably silver behenate or silver stearate, is reduced by an incorporated cyclic organic reducing agent such as the methyl ester of gallic acid in the presence of a toning agent to produce a dense black image. The color-forming layer is clarified by the application of a polymeric overcoat such as cellulose acetate.

This art also teaches that resin binders suitable for the carrier system of the materials described are only those which are soluble in organic solvents such as methyl ethyl ketone, acetone, and heptane. The use and disposal of organic solvents, however, raises environmental and worker safety concerns. These solvents are inherently flammable or explosive and their use requires specially-

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adapted and expensive manufacturing equipment. In addition, they are effluents of the manufacturing process and must be recovered or burned, which adds to the cost of manufacture.

Furthermore, the single sheet transparency compositions commercially available for use in direct thermal printing applications cause sticking of the imaging material to the print head, and have had insufficient sensitivity or thermal response characteristics to produce an adequately dense black output. In addition, commercially available compositions exhibit low maximum density (D-max), high minimum density (D-min), and high light scatter or haze.

Thus, the problem to be solved by this invention is to provide thermal imaging materials which can be manufactured safely and with no adverse environmental impact; which will produce images of great clarity with little haze, very high maximum density, and low minimum density; and which will not stick to the print head nor cause melted material to accumulate on the print head.

#### Summary of the Invention

The aforementioned problem is solved by this invention which provides a multilayer heat-sensitive material which comprises:

a color-forming layer comprising:

a color-forming amount of finely divided, solid colorless noble metal or iron salt of an organic acid distributed in a carrier composition;

a color-developing amount of a cyclic or aromatic organic reducing agent, which at thermal copy and printing temperatures is capable of a color-forming reaction with the noble metal or iron salt; and

an image-toning agent;

characterized in that (a) the carrier composition comprises a substantially water-soluble polymeric carrier and a dispersing agent for the noble metal or iron salt and (b) the material comprising a protective overcoating layer for the color-forming layer.

The color-forming layer of the heat-sensitive material is formed from an aqueous, heat-sensitive composition having a carrier composition comprising a water-soluble polymeric carrier and a dispersing agent. As a result, the layer

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exhibits improved imaging characteristics when used in infrared copying machines, as well as in commercially available direct thermal printing devices such as wide format direct thermal plotters. As previously indicated, the color-forming layer also comprises a color-forming amount of a finely divided, solid colorless noble metal or iron salt of an organic acid; a color-developing amount of a cyclic or aromatic organic reducing agent; and an image-toning agent.

The protective overcoat layer in the multilayer heat-sensitive material of this invention can be formed from a variety of compositions, but a particularly effective composition is a radiation-curable composition comprising one or more reactive monomers that when sufficiently cured will melt, soften, or decompose only at temperatures greater than those attained by commercially available thermal print heads or infrared copy machines. The overcoat layer can be formed using a composition that further includes one or more photoinitiators capable of sufficiently polymerizing the reactive monomers, a dry lubricant, and a mildly abrasive filler.

The multilayer material may also include an intermediate layer comprising a substantially water-soluble or dispersible polymeric material capable of promoting adhesion between the color-forming layer and the protective overcoat layer.

Each of these features of the invention will be described in greater detail hereinafter.

#### Brief Description of the Drawing

The sole drawing illustrates in cross section one embodiment of a multilayer heat-sensitive material of the invention, for example, a heat-sensitive film or paper.

#### Detailed Description of the Invention

Referring to the drawing, the embodiment 10 comprises substrate or support 12, which may be, for example, paper, glass, or a plastic sheeting or film. Suitable film-forming plastic substrates are, for example, poly(ethylene terephthalate), polyolefin, polycarbonate, polysulfone, polystyrene, and cellulose acetate. Support 12 can be transparent, translucent, or opaque. Support 12

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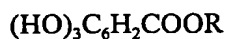
typically is provided with adhesion or subbing layer 14. One or more backing layers 16 may be provided to control physical properties such as curl or static. An example of a suitable support is a commercially available 2.65-mil (0.067 mm) poly(ethylene terephthalate) film support subbed on one side and carrying on the other side an antistatic coating showing a resistance of about  $2 \times 10^{10}$  ohms. Carried by subbing layer 14 is color-forming layer 18 comprising a heat-sensitive coated composition. Tie layer 20 can be optionally included to improve adhesion between color-forming layer 18 and protective, clarifying overcoat 22.

In the color-forming layer the preferred color-forming metal organic acid salt is silver behenate since it is colorless, stable toward light and insoluble in an aqueous vehicle. Silver stearate may be successfully substituted for silver behenate. Silver and gold salts of many other organic acids have also been found useful in heat-sensitive compositions and copying papers, as previously described, for example, in United States Patent No. 3,080,254. A partial list of organic acids suitable for use in the present invention includes oleic, lauric, hydroxystearic, acetic, phthalic, terephthalic, butyric, m-nitrobenzoic, salicylic, phenylacetic, pyromellitic, p-phenylbenzoic, undecylenic, camphoric, furoic, acetamidobenzoic and o-aminobenzoic. While such noble metal salts are preferred in the practice of this invention, the use of corresponding salts of iron can be used in applications where slight background color is acceptable.

Reducing agents which have been found useful in the practice of this invention include: pyrogallol; 4-azeloil-bis-pyrogallol; 4-stearoyl pyrogallol; galloacetophenone; di-tertiary-butyl pyrogallol; gallic acid anilide; methyl gallate; ethyl gallate; normal- and iso-propyl gallate; butyl gallate; dodecyl gallate; gallic acid; ammonium gallate; ethyl protocatechuate; cetyl protocatechuate; 2,5-dihydroxy benzoic acid; 1-hydroxy-2-naphthoic acid; 2-hydroxy-3-naphthoic acid; phloroglucinol; catechol; 2,3-naphthalene diol; 4-lauroyl catechol; sodium gallate; protocatechualdehyde; 4-methyl esculetin; 3,4-dihydroxy benzoic acid; 2,3-dihydroxy benzoic acid; hydroquinone; 4,4'-dihydroxy biphenyl; 3-4-dihydroxyphenylacetic acid; 4-(3',4'-dihydroxyphenylazo)benzoic acid; 2,2'-methylene bis-3,4,5-trihydroxybenzoic acid; ortho- and para-phenylene diamine; tetramethyl benzidine; 4,4',4''-diethylamino triphenylmethane; o-, m-, and

p-aminobenzoic acids; alpha and beta naphthols; 4-methoxy, 1-hydroxy-dihydronaphthalene; and tetrahydroquinoline. Such reducing agents are cyclic or aromatic compounds having an active hydrogen atom attached to an atom of carbon, oxygen or nitrogen which in turn is attached to an atom of the ring. They are capable of causing the reduction of noble metal or iron ions and precipitation of metallic metals.

Particularly useful organic reducing agents are those which are alkyl esters of gallic acid, for example, methyl, ethyl, propyl, octyl, dodecyl and cetyl esters. Especially are ethyl, propyl and octyl esters. These gallic esters conform to the general formula:



where R is an alkyl radical.

The amount of color-forming noble metal or iron salt and organic reducing agent will vary, largely depending upon the particular metal salt being used and the desired shade and intensity of color in the produced colored marks. Generally, the amount of color-forming metal salt present in the composition of the color-forming layer will vary from 10% to 60%, by weight, often from 25% to 40%, and most often from 30% to 35%, on a percent solids basis, i.e., without taking into account the water in which the composition is ultimately dissolved or dispersed. The amount of organic reducing agent in the composition of the color-forming layer will generally vary from 2% to 25%, by weight, often from 3% to 10% and most often from 4% to 8%, on a percent solids basis.

Both the color-forming salt and the organic reducing agent are homogeneously distributed through the composition. The metal salt is in finely divided form, normally as particles having a size of from 0.5 to 10 micrometers and often 1 to 3 micrometers.

The organic reducing agents normally have limited solubility in water, a major obstacle to previous attempts at formulating aqueous carrier compositions. For example, the octyl ester of gallic acid has a solubility of .001g/100g water while the ethyl ester of gallic acid has a solubility of at .6g/100g

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water. An important aspect of this invention is that by dispersing the organic reducing agent in an aqueous solution of a water-soluble polymeric carrier material such as polyvinyl alcohol, and incorporating a dispersing agent typically used for the fine grinding of developers used in the manufacture of direct thermal printing papers, and then subjecting the resulting dispersion to mild heating, e.g. a temperature of 130° F (55°C), a clear solution can be obtained. Such a solution is stable at room temperature for a considerable period, e.g. 24 to 72 hours.

The above aspect of this invention is illustrated by the results reported in the following Table I. Such results were obtained using a propyl gallate reducing agent with carrier materials having the compositions indicated. The polymeric carrier material used was partially hydrolyzed (87-89%) polyvinyl alcohol, commercially available as Airvol 203 from Air Products and Chemicals, Inc., Allentown, PA. The dispersing agent used was an ammonium salt of styrene/acrylic acid copolymer, commercially available as Lupasol FF-3249 from BASF Corp., Parsippany, NJ.

TABLE I

	<u>Solution g/100g*</u>	<u>Solution Life(hrs)</u>	<u>Solution Appearance (24 hr.)</u>
Solution A: Water Only	.35	0	moderately cloudy
Solution B: Polyvinyl Alcohol (20% solution in water) Only	2.20	>1 wk	virtually clear
Solution C: Dispersing Agent (35% solution in water) Only	2.20	2 hr	moderately cloudy
Solution D: Polyvinyl Alcohol/ Dispersing Agent (25% solution of Polyvinyl Alcohol/ Dispersing Agent (2.5:1) mixture in water)	4.40	72 hr	virtually clear

\*Grams of propyl gallate reducing agent in 100 grams of deionized water.

As can be seen from Table I, only Solution D, the combination of the dispersing agent, polyvinyl alcohol and propyl gallate, provides a stable solution



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at maximum solubility for the propyl gallate reducing agent. Increasing the solubility of propyl gallate, as obtained in Solution D versus with polyvinyl alcohol alone in water or dispersing agent alone in water is significant in that, among other benefits, greater flexibility to vary the amount of carrier material and, therefore, to vary the coating conditions, is achieved without deleterious effects on sensitivity. Accordingly, increased sensitivity can be achieved using the same or lower amounts of the carrier material, and heat-sensitive materials having excellent clarity can be obtained.

The relative amounts of polyvinyl alcohol polymeric carrier and ammonium salt of styrene/acrylic acid copolymer dispersing agent can vary from 50% to 90% polyvinyl alcohol (i.e. 10% to 50% ammonium salt of styrene/acrylic acid copolymer), often 60% to 70% polyvinyl alcohol (i.e. 40% to 30% ammonium salt of styrene/acrylic acid copolymer). Use of less than a solubility enhancing amount of dispersing agent may result in an insufficient quantity of propyl gallate in solution. Conversely, an insufficient concentration of polyvinyl alcohol will result in premature precipitation of the propyl gallate.

Phthalazone, also known as phthalazinone, is conveniently used as a toning agent and is fully described in the prior art, as illustrated by United States Patent No. 3,080,254 previously mentioned herein. Other suitable materials that can be used as toning agents include barbituric acid, 2-benzoxazolethiol, and l-acetal-2-thiohydantoin, which are also well known in the art.

Generally, the amount of phthalazone in the color-forming layer can be from 2% to 25%, by weight, often from 3% to 15%, and most often from 4% to 6%. In these amounts, the weight ratio of the noble metal or iron salt to phthalazone will be between 4:1 to 8:1 with a weight ratio of 6:1 being most suitable. The phthalazone is preferably ground with the noble metal or iron salt to a particle size of from 0.5 to 10 micrometers and often 1 to 3 micrometers.

The carrier composition in which the noble metal or iron salt, organic reducing agent and phthalazone are distributed comprises one or more substantially water-soluble, fully or partially-hydrolyzed grades of polyvinyl alcohol. The degree of hydrolysis is normally from 87% to 89%. The viscosity of

the composition can be readily adjusted to any level by varying the amount of polyvinyl alcohol or by selection of higher or lower molecular weight.

Other water-soluble polymeric materials suitable for use with or in place of the polyvinyl alcohol carrier material in this invention include methyl  
5 cellulose, carboxy methyl cellulose, polysaccharide gums, gelatins, styrene butadiene copolymers, hydroxylated corn starch, acrylic latexes, vinyl acetate copolymers, and blends or mixtures thereof. Generally, the total amount of carrier in the composition of the color-forming layer will be 10% to 60%, by weight, often 25% to 50%, and most often 40% to 50%.

10 The coating composition may also include common wetting agents, surfactants, and various additional components for enhancing the properties of the composition such as antifoggants, coating aids, and hardeners for the polyvinyl alcohol or other carrier materials.

Suitable antifoggants for use in this invention are well-known  
15 photographic antifoggants such as 2-mercaptobenzo-triazole, chromate, oxalate, citrate, carbonate, benzotriazole (BZT), 5-methylbenzotriazole, 5,6-dimethylbenzotriazole, 5-bromobenzotriazole, 5-chlorobenzotriazole, 5-nitrobenzotriazole, 4-nitro-6-chlorobenzotriazole, 5-nitro-6-chlorobenzotriazole, 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, benzimidazole, 2-methylbenzimidazole,  
20 5-nitrobenzimidazole, 1-phenyl-5-mercaptopotetrazole (PMT), 2-mercaptobenzimidazole, 2-mercaptobenzothiazole, 2-mercaptobenzoxazole, 2-mercaptothiazoline, 2-mercapto-4-methyl-6,6'-dimethylpyrimidine, 1-ethyl-2-mercapto-5-amino-1,3,4-triazole, 1-ethyl-5-mercapto-1,2,3,4-tetrazole, 2,5-dimercapto-1,3,4-thiodiazole, 2-mercapto-5-amino-1,3,4-thiodiazole,  
25 dimethyldithiocarbamate, and diethyldithiocarbamate. Antifoggants having relatively low solubility are useful, particularly those having a  $pK_{sp}$  of from 14 to 20.

Boric acid is an example of a suitable hardener for carrier materials such as polyvinyl alcohol. Other suitable hardener and crosslinking materials are  
30 well known to those skilled in the art.

Surfactants and wetting agents, such as FC-129 surfactant (an anionic fluoro-surfactant consisting of 50% potassium fluoroalkyl carboxylates

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dissolved in 2-butoxyethanol, ethyl alcohol and water, commercially available from 3M Industrial Chemical Products Division, St. Paul, MN) may also be incorporated into the coating composition to prevent repellency defects such as "fisheyes" or spots. Such surfactants can be present in the composition of the color-forming layer at a concentration of from 0.01% to 0.5%, based on the weight of the composition.

The total concentration of the aforementioned and other addenda in the final coating composition can range from 0.01% to 5% of the composition on a percent solids basis. By "percent solids basis" is meant the weight percent based on the combined weight of the non-aqueous components of the coating composition. Depending on the particular materials employed, the various addenda may be incorporated in or ground with the color-forming metal salt and other components to be finely divided, or dissolved in the solution or dispersion of the carrier material in water. For example, the silver salt, toning agent and other materials to be finely ground are mixed and ground together in a dispersion or solution of the carrier material in water. The silver salt composition is ground to an average particle size of from 0.5 to 3  $\mu\text{m}$ . As described hereinbefore, the reducing agent is dissolved in a solution of polyvinyl alcohol, dispersing agent, and water. The resulting silver salt grind and reducing agent compositions are then mixed together into a single coating composition which can be applied to a support optionally after being further diluted with water. The total amount of water present in the color-forming layer coating composition can range from 40% to 95%, often 60% to 85%, by weight.

The color-forming layer coating composition can be coated at a coating flow rate to yield a dried coverage of from 0.5 to 3.0 lb/MSF (2.4 to 14.6  $\text{g}/\text{m}^2$ ), often from 0.9 to 2.2 lb/MSF (4.4 to 10.7  $\text{g}/\text{m}^2$ ). By "lb/MSF" is meant pounds per 1000 square feet. The composition is coated and passed through a drying tunnel at a rate of 100 to 200 feet per minute (0.5 to 1 m per sec.), at a drying temperature of from 140 to 200°F (60 to 93°C), depending upon the coating speed. The water is evaporated from the coating leaving color-forming layer 18 adhered to subbing layer 14 and thereby to support 12, as depicted in the drawing. When using a plastic support any suitable, compatible material may be used as

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listed hereinbefore. Alternatively, the color-forming layer coating composition may be applied to paper or other support.

As previously stated, the compositions used in the practice of the invention may be used in films suitable for thermal copying as well in direct thermal printing films comprising (1) a substrate or support formed from a flexible material, (2) a color-forming layer of the thermally imageable composition applied to at least one surface of the substrate, (3) an optional intermediate layer capable of promoting intercoat adhesion between the color-forming layer and (4) a protective, clarifying overcoat having sufficient hardness and frictional properties to allow for direct thermal recording. In this embodiment, the composite layers produce a film transparent to visible, UV and infrared light. The coated layers are sufficiently flexible that the substrate bearing them can be imaged in commercially available infrared copying machines and can be wound into rolls or used as sheets in commercially available direct thermal printing devices.

As previously stated, a significant feature of the invention is that the combination of polyvinyl alcohol or equivalent water-soluble polymeric material, dispersing agent, and water as described herein, totally dissolves the organic reducing agent, greatly increasing the clarity of the finished product and improving its imaging characteristics due to the intimate relationship of the solution to the noble metal or iron salt in dispersion. The D max exhibited by the multilayer heat-sensitive material of the invention is greater than can be achieved with comparable materials wherein the organic reducing agent is in particulate form.

As previously indicated herein, for some applications it has been found useful to incorporate an intermediate layer or "tie" coat that promotes adhesion between the color-forming layer and the protective overcoat. The use of an intermediate layer is particularly useful to avoid polymer incompatibility that can occur when adhesion promoting resins are added to the color-forming layer. Styrene/butadiene copolymers are especially useful for this purpose. Other materials that work well are polyvinyl acetate copolymers, and polyurethanes. Generally, the concentration of the intermediate layer adhesion-promoting material will vary from 5% to 50%, by weight in deionized water, often from 10% to 20%

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and most often from 15% to 18%. The intermediate layer may also contain wetting agents, surfactants and various additional components for enhancing properties of the composition. Other conventional materials or additives that promote adhesion can also be included in the composition without departing from the spirit of the invention. Similarly, these additives or materials can be added directly to the color-forming layer and be considered within the scope of the invention.

The use of a protective overcoating layer serves multiple purposes. The overcoat in the present invention functions to achieve maximum optical clarity. It also provides protection for the color-forming layer. The overcoat protects the color-forming layer from fingerprinting and abrasion when the transparency sheets are handled in normal use, as well as from exposure to the elements, particularly moisture at elevated temperature and humidity. An overcoating layer resistant to various common hazards is highly beneficial to the user. Materials appropriate for overcoating layers provide not only clarity and protection from the elements, but they also fulfill other important requirements such as being environmentally safe or solvent free, having good frictional properties which relate to feed properties in various thermal printing devices, and non-sticking properties both to thermal print heads and to various laser-or toner-based originals. Obviously, the overcoating layer must not hinder or retard the imaging characteristics. Also, the overcoat must be chemically compatible with the underlying color layer and must not cause premature color formation.

It has been determined that radiation curable materials, as described herein, are particularly effective in providing the above desired characteristics and requirements. The resins selected offer superior optical clarity and exhibit exceptional protection, particularly from moisture and heat. The non-overcoated color-forming layer typically appears hazy. This is thought to result from light scattering at the surface of the color-forming layer. The addition of a protective overcoating layer according to the invention yields a heat-sensitive material of exceptional optical clarity. In this regard, radiation-curable overcoats are markedly superior to non-cured overcoats. Since radiation curable coatings are typically

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manufactured and coated as a liquid at 100% solids, they are solvent-free, and thereby enjoy the safety and cost benefits noted hereinbefore.

Sticking of the image-forming material against a hot print head can be prevented by the selection of monomers or oligomers of varying molecular weight and composition to control hardness, flexibility, and melting or softening point. It is also possible to eliminate sticking by selecting polymers for use in the protective layer which have no glass transition temperature ( $T_g$ ) or melting point ( $T_m$ ), but which decompose without residue. Selection of the photoinitiator also must be based on degree of cure or polymerization required for the particular application.

A suitable radiation-curable overcoat composition can comprise one or more acrylic or vinylic monomers, a photoinitiator and typically a wetting agent. Other materials, such as surfactants, slip agents, dry lubricants, mar resistance agents, and inert fillers may be included in order to enhance the properties of the overcoat layer.

Examples of suitable slip agents, which also increase the mar resistance of the overcoat layer, are silicone compounds such as modified or unmodified dimethyl polysiloxanes, including the polyether modified, polyester modified, and polyester modified reactive dimethylpolysiloxanes of the type sold by BYK-Chemie USA of Wallingford, Connecticut under the trademarks BYK®-300, -301, -302, -307, -310, -320, -321, -322, -325, -330, -331, -336, -341, -344, -351, -370, -085. Other suitable materials include acrylic and methacrylic functional silicones commercially available as BYK®-371 from BYK Chemie, those available from Hüls America, Inc. of Piscataway, New Jersey under the designations Hüls PS560, PS583, PS802, PS851, PS852, PS853, PS854, PS406, PS901, PS9015, and the product sold by Dow Corning as Additive 28. These and other known slip agents may be used either alone or in combination, at concentrations ranging from 0.05 to 5%, often from 0.05 to 3.0% of the total overcoat composition. Such materials may be incorporated in order to prevent sticking of the imaging member to the thermal print head, as well as to increase the mar resistance of the final product.

Suitable inert filler materials which serve to prevent the accumulation of debris on the print head and to reduce the coefficient of friction for proper transport through the thermal printing apparatus are those which have mild abrasive properties, high oil absorption characteristics, for example in the range of from 40g to 150g oil/100g filler, and an average particle size of about 1.1  $\mu\text{m}$ . Aluminum oxide (alumina) having an average particle size of 1.0 to 5.0  $\mu\text{m}$  is a very useful filler material. Other useful filler materials include barium sulfate, calcium carbonate, clays, silica, titanium dioxide, zinc oxide, talc, chromium oxide, aluminum hydrates, fluorinated polyethylene and microcrystalline waxes. Such filler materials can be present in the overcoat composition at amounts of from 0.5% to 5% by weight, of the total composition, generally from 0.9% to 2% of the total composition.

Suitable dry lubricants in the overcoat composition are metal salts of long-chain aliphatic carboxylates, for example, zinc stearate or calcium stearate.

Examples of suitable radiation-curable monomers include: N-vinyl pyrrolidone, allyl methacrylate, tetrahydrofurfuryl methacrylate, cyclohexyl methacrylate, n-hexyl methacrylate, cyclohexyl acrylate, 2-ethoxyethyl acrylate, 2-ethoxyethyl methacrylate, isodecyl methacrylate, 2-methoxyethyl acrylate, 2(2-ethoxyethoxy) ethylacrylate, stearyl acrylate, behenyl acrylate, nonyl phenol ethoxylate acrylate, tetrahydrofural acrylate, lauryl methacrylate, stearyl methacrylate, octyl acrylate, lauryl acrylate, monomethoxy 1, 6-hexanediol acrylate, monomethoxy tripropylene glycol acrylate, monomethoxy neopentyl glycol propoxylate acrylate, 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate, glycidyl methacrylate, isodecyl acrylate, isobornyl methacrylate, benzyl acrylate, hexyl acrylate, isooctyl acrylate, tridecyl methacrylate, caprolactone acrylate, isobornyl acrylate, triethylene glycol dimethacrylate, ethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, 1,3-butylene glycol diacrylate, 1,4-butenediol diacrylate, 1,4-butanediol dimethacrylate, diethylene glycol diacrylate, diethylene glycol dimethacrylate, 1,6-hexanediol diacrylate, 1,6-hexanediol dimethacrylate, 1,6-hexanediol diglycidyl ether, bisphenol A propoxylate diglycidyl ether, bisphenol A ethoxylate diglycidyl ether, neopentyl glycol propoxylate diglycidyl ether, neopentyl glycol diacrylate, neopentyl glycol

propoxylate diacrylate, neopentyl glycol dimethacrylate, polyethylene glycol (200) diacrylate, tetraethylene glycol diacrylate, triethylene glycol diacrylate dimethacrylate, 1,3 butylene glycol dimethacrylate, tripropylene glycol diacrylate, ethoxylated bisphenol A dimethacrylate, ethoxylated bisphenol A diacrylate, bisphenol A propoxylate diacrylate, tris (2-hydroxyl ethyl) isocyanurate trimethacrylate, pentaerythritol tetraacrylate, trimethylpropane trimethacrylate, trimethylpropane triacrylate, trimethylpropane propoxylate triacrylate, glyceryl propoxylate triacrylate, trimethylpropane ethoxylate triglycidyl ether, tris (2-hydroxy ethyl) isocyanurate triacrylate, dipentaerythritol pentaacrylate, pentaerythritol triacrylate, ethoxylated pentaerythritol tetraacrylate, polyethylene glycol (600) dimethacrylate, polyethylene glycol (600) diacrylate, polyethylene glycol (400) diacrylate, polypropylene glycol monomethacrylate, polypropylene glycol monoacrylate, ditrimethylpropane tetraacrylate, ethoxylated trimethylpropane triacrylate, propoxylated trimethylpropane triacrylate, propoxylated neopentyl glycol diacrylate, glyceryl propoxy triacrylate, propoxylated glyceryl triacrylate, pentaacrylate ester, alkoxylated aliphatic diacrylate ester, alkoxylated trifunctional acrylate, trifunctional methacrylate ester, trifunctional acrylate ester, aliphatic monofunctional ester, aliphatic difunctional ester, alkoxylated diacrylate ester, polybutadiene diacrylate, aliphatic urethane acrylate, aromatic urethane acrylate, epoxy acrylate, bisphenol A epoxy diacrylate, and polyester acrylate.

Examples of suitable photoinitiators include: benzyldimethyl ketal, trimethylbenzophenone, isopropylthioxanthone, ethyl 4-(dimethylaminobenzoate), benzophenone, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, 2,2 dimethoxy-2-phenylacetophenone, 2,2 dimethoxy-1,2-diphenyl ethanone, 2-hydroxy-2-methyl-1-phenyl propanone, and 2-methyl-1-(4-(methylthio)phenyl)-2-morpholinopropanone-1. 1-hydroxycyclohexyl phenyl ketone is particularly effective. The amount of the photoinitiator can range from 2% to 30%, by weight, often from 2% to 15% and most often from 5% to 10% of the coating compositions.

Other conventional additives, such as wetting and dispersing agents or materials commonly used in heat-sensitive compositions other than those previously mentioned, can also be included in the protective overcoat composition.



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The overcoat composition may be applied to the color-forming layer or to an intermediate layer that has been applied to the color-forming layer at a coating rate to yield a dry coverage of from 0.2 to 1.0 lb/MSF (1 to 5 g/m<sup>2</sup>), often from 0.50 to 1.0 lb/MSF (2.4 to 5 g/m<sup>2</sup>).

5                   Following application of a radiation-curable overcoat composition curing can be achieved using any suitable means, for example, by passing the coated member through a conventional ultraviolet processor, such as an Aetek UV XL processor at a rate of 100 to 200 feet per minute (0.5 to 1 m/sec). At 100 feet per minute (0.5 m/sec.) the overcoat composition described in the following  
10                   Example 1 requires approximately 50 mj of energy to polymerize completely. One UV lamp at 300 watts per inch (2.54 cm) will achieve this energy level. Higher line speeds can be accomplished by using more lamps and increased wattage. Alternatively, conventional electron-beam curing can be employed.

15                   U.S. Patents 3,080,254, 3,031,329, 3,446,648 and 5,026,606, previously cited herein, describe various prior art compositions, structural configurations and process techniques known to the art which may be used with the present invention.

                  The following Examples are presented to further illustrate the invention.

#### 20                   Example 1

##### Heat-Sensitive Color-Forming Layer

                  An aqueous heat-sensitive composition for thermal imaging devices is made as follows: A color-forming suspension (Mix 1) of solids having the  
25                   following composition was prepared by grinding the listed ingredients at a concentration of about 20%, by weight, in deionized water to a particle size of 1 to 3 micrometers to form a dispersion of silver behenate and phthalazone in an aqueous solution of polyvinyl alcohol.

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Mix 1

	<u>Dry Weight %</u>
Silver Behenate	58.72
Phthalazone	9.02
Polyvinyl Alcohol*	32.26

A color-developing mixture (Mix 2) of solids having the following composition was prepared by dispersing and blending the ingredients at 130°F (55°C) at a concentration of about 18%, by weight, in deionized water until all solids were dissolved.

Mix 2

	<u>Dry Weight %</u>
Propyl Gallate	23.40
Polyvinyl Alcohol*	54.42
Ammonium Salt of Styrene/Acrylic Acid Copolymer**	22.18

A solution of polyvinyl alcohol carrier vehicle in water (Mix 3) was prepared by dissolving polyvinyl alcohol in deionized water to form a solution having a concentration of about 22%, by weight of polyvinyl alcohol.

\*The polyvinyl alcohol used in this and the following Example was 87-89% hydrolyzed polyvinyl alcohol, commercially available as Airvol 203 from Air Products and Chemicals Inc., Allentown, PA.

\*\*The ammonium salt used in this and the following Example is commercially available as Lupasol FF-3249 dispersing agent from BASF Corp., Parsippany, NJ.

The three mixes (Mixes 1, 2, and 3) were then blended together in equal parts to give a final heat-sensitive coating composition having the following formula:

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	<u>Dry Weight %</u>
Silver Behenate	36.90
Phthalazone	6.43
Propyl Gallate	6.76
5 Ammonium Salt of Styrene/Acrylic Acid Copolymer	6.41
Polyvinyl Alcohol	43.50

10 The composition formed was applied to a clear 2.65 mil  
(0.067 mm) polyethylene terephthalate film support. The coated composition was  
dried at 140°F (60°C). Two sets of coated samples at different coverages were  
prepared for further coating and later testing: Sample A, 0.9 lb/MSF (4.4 g/m<sup>2</sup>)  
and Sample B, 2.2 lb/MSF (10.7 g/m<sup>2</sup>), dry coverages.

15

#### Intermediate Adhesion or Tie Layer

An intermediate tie layer coating composition was prepared by  
dissolving a styrene/butadiene copolymer (commercially available under the trade  
name Styrofan ND 593 from BASF Corp., Parsippany, NJ) in deionized water to  
20 form a solution having a concentration of about 10%, by weight, of copolymer in  
water. This composition was applied to a length of each of the color-forming  
layers described previously (Samples A and B) at coverages between 0.02 and 0.15  
lb/MSF (0.098 and 0.73 g/m<sup>2</sup>), dry coverage. The resulting samples were  
identified as Samples AC and BC, respectively.

25

#### Protective Overcoating Layer

A radiation-curable overcoat formulation designated Mix E and  
having the following composition was prepared:

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Mix E

		<u>Weight %</u>
5	Monomer A (1,6-Hexanediol Diacrylate)	27.30
10	Monomer B (Dipentaerythritol Hydroxy- Penta Acrylate)	63.60
15	Photoinitiator (2-Hydroxy-Methyl-1-Phenyl Propanone)	8.20
	Wetting Agent	.90

20 This composition was applied at a coverage of 0.60lb/MSF  
(2.9 g/m<sup>2</sup>) to each of Samples A, B, AC, and BC, resulting in four structures  
identified as AE, BE, ACE, and BCE, having two levels of color-forming layer  
coverage, and presence or absence of an intermediate tie layer. These overcoated  
samples were radiation cured by exposure to an ultraviolet source of 50 mj  
intensity per cm<sup>2</sup> to provide protective overcoating layers for the respective color-  
25 forming layers.

The imaging and keeping properties of the multilayer heat-sensitive  
film materials made according to this Example 1 were measured, and the results  
reported in the following Table II. The transmission density was measured for  
nonimaged or unexposed areas ( $D_{min}$ ) and for imaged or exposed areas to provide  
30 maximum density values ( $D_{Max}$ ). More specifically, the data in Table II was  
obtained by imaging samples on a heated metal block at 300 degrees F (149°C).  
The value obtained at 300 degrees F (149°C) is the reported D max value, whereas  
the unimaged or area not subjected to 300 degrees (149°C) is the reported D min  
value. The data or value recorded is a direct reading from the densitometer used.  
35 This was a commercially available densitometer (X-RITE, Model 361T  
transmission densitometer).

Table II shows data from samples prepared as described in this Example 1, as well as from identical samples aged for 24 hours at 60°C and ambient RH ("Heat"), and for 24 hours at 50°C at 65% RH ("Heat and Moisture").

TABLE II

<u>Sample Structure</u>	<u>As Coated</u>		<u>Heat</u>		<u>Heat and Moisture</u>	
	$D_{\min}$	$D_{\max}$	$D_{\min}$	$D_{\max}$	$D_{\min}$	$D_{\max}$
AE	.06	1.45	.07	1.55	.08	1.55
BE	.09	3.50	.10	4.00	.14	4.00
ACE	.06	1.45	.07	1.55	.08	1.55
BCE	.09	3.50	.10	4.00	.14	4.00

The values reported in the above Table II demonstrate that the heat-sensitive materials of this invention exhibit excellent image formation and clarity (high  $D_{\max}$ , low  $D_{\min}$ ) which are substantially maintained upon aging under the conditions described. Also, in comparisons with a commercially available heat-sensitive transparency film in both infrared imaging and direct thermal printing using conventional equipment, it was found that the materials prepared as described in this Example 1 exhibited superior properties, including improved release from the originals and substantially no tendency to stick to print heads while the commercially available films exhibited a great tendency to stick to such heads.

### Example 2

Heat-sensitive materials were prepared according to Example 1 using the following heat sensitive and protective overcoating compositions.

The heat-sensitive coating formulation had the following composition:

<u>Component</u>	<u>% Solids</u>
Silver Behenate	32.28
Polyvinyl Alcohol	46.88

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	Phthalazone	4.94
	Mercaptobenzotriazole	0.76
	Boric Acid	1.92
5	Ammonium Salt of Styrene/ Acrylic Acid Copolymer	6.40
	Propyl Gallate	6.75
	FC-129 surfactant	0.07

10 This composition was prepared by the method of Example 1 and  
diluted to a concentration of 20% of the above combination of components in water  
for a coating composition as follows:

	<u>Component</u>	<u>% Solids</u>
	Water	80.000
15	Silver Behenate	6.456
	Polyvinyl Alcohol	9.376
	Phthalazone	0.988
	Mercaptobenzotriazole	0.152
	Boric Acid	0.384
20	Ammonium Salt of Styrene/ Acrylic Acid Copolymer	1.280
	Propyl Gallate	1.350
	Surfactant*	0.014

25 \*Available from 3M Industrial Chemicals Products Division, St. Paul, MN as FC-  
129 surfactant.

The resulting image-forming composition was coated at a dried weight of 2.2  
lb/MSF (10.7 g/m<sup>2</sup>).

30 The overcoating composition was as follows:

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	<u>% Solids</u>
Pentacrythritol Triacrylate	71.42
1-Hydroxycyclohexyl phenyl ketone	6.26
N-Vinyl pyrrolidone	17.71
5     Calcium stearate	2.78
Aluminum oxide	1.83

The composition was coated at a weight of 0.55 lb/MSF (2.68 g/m<sup>2</sup>). Upon evaluation of the resulting heat-sensitive materials using the procedures set forth in Example 1; such materials exhibited the same combination of excellent image formation and clarity (high  $D_{\max}$  and low  $D_{\min}$ ) described in Example 1.

It is evident from the foregoing description, particularly the illustrative Examples, that the present invention provides multilayer heat-sensitive materials suitable for thermal imaging that can be manufactured safely and with no adverse environmental impact; which produce images of great clarity with little haze, very high maximum density, and low minimum density; and which will not stick to print heads nor cause melted materials to accumulate on print heads of the type used in conventional direct thermal imaging devices. The invention enables manufacture of color-forming materials without organic solvents. This process provides for a solution in water of primary developer materials that were previously found to be insoluble in water. Due to the importance of protecting the environment, and the greater safety associated with aqueous versus organic solutions, the invention is believed to provide a significant positive environmental impact.

As previously indicated herein, an embodiment of the invention is depicted in the sole drawing of a multilayer heat-sensitive material where the components are identified as follows:

10 . . . multilayer heat-sensitive material, 12 . . . support, 14 . . .  
 subbing layer, 16 . . . backing layer, 18 . . . color-forming layer, 20 . . . tie layer,  
 22 . . . protective overcoating layer.

CLAIMS:

1. A multilayer heat-sensitive material which comprises:  
a color-forming layer comprising:  
5 a color-forming amount of finely divided, solid colorless noble metal or iron salt of an organic acid distributed in a carrier composition;  
a color-developing amount of a cyclic or aromatic organic reducing agent, which at thermal copy and printing temperatures is capable of a color-forming reaction with the noble metal or iron salt; and  
10 an image-toning agent;  
characterized in that (a) the carrier composition comprises a substantially water-soluble polymeric carrier and a dispersing agent for the noble metal or iron salt and (b) the material comprises a protective overcoating layer for the color-forming layer.
- 15 2. A material of claim 1 in which the noble metal salt comprises silver behenate, the reducing agent comprises propyl gallate and the toning agent comprises phthalazone.
- 20 3. A material of claim 1 in which the dispersing agent comprises an ammonium salt of styrene/acrylic acid copolymer.
4. A material of claim 1 wherein the protective overcoating layer is formed from a radiation-curable composition.
- 25 5. A material of claim 4 wherein the radiation-curable composition comprises an acrylate, glycidyl or vinylic monomer, a dry lubricant, and a filler.
- 30 6. A material of claim 5 wherein the dry lubricant is zinc stearate or calcium stearate.



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7. A material of claim 6 wherein the filler is barium sulfate, calcium carbonate, a clay, silica, titanium dioxide, zinc oxide, aluminum oxide, talc, chromium oxide, an aluminum hydrate, fluorinated polyethylene or a microcrystalline wax.

8. A material of claim 1 which further comprises an adhesion-promoting layer between the color-forming layer and the protective overcoating layer.

9. An aqueous heat-sensitive composition suitable for use in forming the multilayer heat sensitive material of claim 1 which comprises:

a color-forming amount of finely divided,  
silver behenate;

a color-developing amount of a cyclic organic reducing  
agent, which at thermal copy and printing temperatures is capable of a  
color-forming reaction with the silver behenate;

an image-toning amount of phthalazone; and  
an aqueous carrier composition for the silver behenate and  
organic reducing agent which comprises a substantially water-soluble  
partially-hydrolyzed polyvinyl alcohol and an ammonium salt of styrene/acrylic  
acid copolymer dispersing agent; the components being present in the following  
amounts:

Weight % Solids

Silver Behenate	25-40
Phthalazone	3-15
Reducing Agent	3-10
Ammonium Salt of	
Styrene/Acrylic Acid Copolymer	5-10
Polyvinyl Alcohol	25-50

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10. A method for forming an aqueous heat-sensitive composition suitable for forming the multilayer heat-sensitive material of claim 1, which comprises:

(a) forming a color-forming dispersion having the following composition, prepared by grinding in a concentration of 10%-40%, by weight, in water, to a particle size of 0.5 to 10 micrometers:

Weight % Solids

Silver Behenate	10-60
Phthalazone	2-25
Polyvinyl Alcohol	10-60

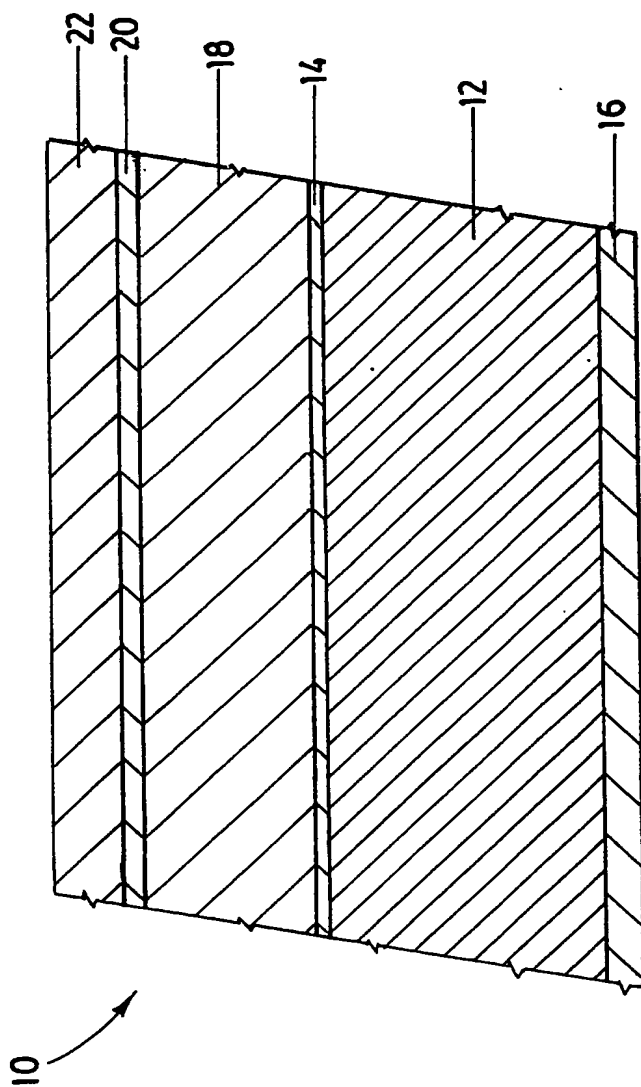
(b) forming a color-developing solution having the following composition, prepared by dispersing and blending the following materials at about 55°C in a mix until dissolved in a concentration of 10-30%, by weight, in water:

Weight % Solids

Propyl Gallate	5-25
Polyvinyl Alcohol	10-60
Ammonium Salt of Styrene/Acrylic Acid Copolymer	3-25

(c) mixing the dispersion of (a) and solution of (b) together to form an aqueous heat-sensitive coating composition.

1/1



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/00615

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(5) : G03C 1/38, 1/494, 1/498 US CL : 430/338, 341, 523, 617, 618 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 430/338, 341, 523, 617, 618 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,031,329 (WINGERT) 24 April 1962, column 4, lines 4-75.	1-10
Y	US, A, 5,057,570 (MILLER ET AL) 15 October 1991, column 6, claim 5.	1-10
Y	US, A, 4,460,727 (SHOJI) 17 July 1984, column 2, lines 13-60.	3, 9, 10
Y	US, A, 4,353,980 (HELLING ET AL) 12 October 1982, column 3, lines 18-35; column 4, lines 15-20; column 5, lines 40-56; column 6, lines 45-50.	5, 7
Y	Research Disclosure, (Kenneth Mason Publication), December 1989, pages 993-1013, Sections IX, XI, XII and XVI.	1, 5-7
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be part of particular relevance "E" earlier document published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family	
Date of the actual completion of the international search 21 MARCH 1994		Date of mailing of the international search report APR 04 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer THORL CHEA Telephone No. (703) 308-2351